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(54) Interfacial viscosification of aqueous systems utilizing sulphonated ionomers.

(57) The present invention relates to a process for the viscosification of an aqueous liquid which includes the steps of forming a solvent system of an organic liquid or oil and a polar cosolvent, the polar cosolvent being less than about 10 weight percent of the solvent system, the viscosity of the solvent system being less than 1000 cps; dissolving a neutralized sulfonated polymer in the solvent system to form a solution, the concentration of the neutralized sulfonated polymer in the solution being 0.01 to 0.5 weight percent, the viscosity of the solution being less than 200 cps. Thereafter said solution is admixed or contacted with 5 to 500 volume percent aqueous fluid, the aqueous fluid being immiscible with the organic liquid and with the polar cosolvent wherein the neutralized sulphonated polymer transfers from the organic liquid to the aqueous fluid, thereby causing the aqueous phase to thicken.

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3           The present invention relates to a process for  
4 the viscosification of an aqueous liquid which includes  
5 the steps of forming a solvent system of an organic  
6 liquid or oil and a polar cosolvent, the polar cosolvent  
7 being less than 15 weight percent of the solvent system,  
8 the viscosity of the solvent system being less than  
9 1,000 cps; dissolving a neutralized or unneutralized  
10 sulphonated polymer (water insoluble) in the solvent  
11 system to form a solution, the concentration of the  
12 neutralized or unneutralised sulphonated polymer in the solution being  
13 0.01 to 0.5 weight percent, the viscosity of the solution  
14 being less than 200 cps; and admixing or contacting  
15 said solution with 5 to 500 volume percent of the  
16 aqueous liquid which is selected from the group consist-  
17 ing of water and aqueous acid solution, the aqueous  
18 liquid being immiscible with the organic and with the polar  
19 cosolvent wherein the neutralised sulphonated polymer  
20 transfers : from the organic liquid to the aqueous  
21 phase, thereby causing the aqueous phase to gel (i.e.  
22 thicken).

23

24           The present invention relates to a process for  
25 the gelation of an aqueous liquid, wherein the aqueous  
26 liquid is selected from water  
27 and an aqueous acid solution which includes the steps of  
28 forming a solvent system of an organic liquid or oil and  
29 a polar cosolvent, the polar cosolvent being less than  
30 15 weight percent of the solvent system and with the  
31 viscosity of the solvent system being less than 1000 cps, preferably  
32 less than 100 cps. Subsequently a neutralised sulphonated polymer is  
33 dissolved in the solvent system to form a solution with a  
34 concentration of the neutralised sulphonated polymer in the

1 ~~solution being 0.01 to 0.5 weight percent, the viscos-~~  
2 ~~ity of the solution being less than 200 cps. Said~~  
3 ~~solution is admixed or contacted with about 5 to 500 volume~~  
4 ~~percent aqueous liquid, the aqueous liquid being immis-~~  
5 ~~cible with the organic liquid and with the polar cosolvent~~  
6 ~~wherein the neutralized sulphonated polymer transfers from the~~  
7 ~~organic liquid to the aqueous phase, thereby causing the~~  
8 ~~aqueous phase to gel.~~

9           The gelled aqueous phase having a viscosity  
10 greater than 50 cps is formed by the addition of aqueous  
11 liquid to the water insoluble solution which comprises  
12 a water insoluble, neutralised or unneutralised sulphonated polymer,  
13 a nonpolar organic liquid and a polar cosolvent, wherein  
14 the solution has a viscosity less than 200 cps. The  
15 concentration of neutralised or unneutralised sulphonated polymer in  
16 the solution is 0.01 to 0.5 weight percent. Upon the  
17 addition of aqueous liquid to the solution, the polar  
18 cosolvent and water insoluble, neutralised or unneutralised sulphonated  
19 polymer rapidly transfers from the solution to the  
20 aqueous phase which undergoes immediate gelation. The  
21 nonpolar organic liquid can be removed from the gel by  
22 conventional liquid extraction methods. The formation  
23 of the aqueous fluid           having a viscosity of  
24 at least 50 cps from the organic solution having a  
25 viscosity less than 200 cps, can be quite rapid of the  
26 order of           1 minute to 24 hours, more preferably  
27           1 minute to 30 minutes, and most preferably  
28           1 minute to 10 minutes, however, this depends  
29 on temperature, shear, solvent type, etc.

30           The component materials of the present process  
31 generally include a water insoluble, ionomeric polymer  
32 such as a water insoluble, neutralized sulfonated poly-  
33 mer at a critical concentration level of 0.01 to 0.5  
34 weight percent, a nonpolar organic liquid, polar cosol-  
35 vent and water or aqueous acid solution.

1           Gelation of an aqueous phase does not occur,  
2 if one employs a conventional unsulfonated polymer or a  
3 water soluble, neutralized sulfonated polymer in place  
4 of the water insoluble, neutralized sulfonated polymer,  
5 but rather only classical phase separation occurs.

6           In the present invention, the gelation of the  
7 aqueous phase occurs by the formation of geometrically  
8 shaped spheres of the water insoluble, neutralized  
9 sulfonated polymer within the aqueous phase, wherein the  
10 water is encapsulated within these geometrically shaped  
11 spheres (so-called water-in-water pseudo-emulsion).  
12 During the process, approximately 10 weight percent  
13 ~~of the nonpolar organic liquid also transfers to the~~  
14 aqueous phase and is encapsulated within these geo-  
15 metrically shaped spheres.

16           A second aspect of the present invention  
17 relates to the use of these materials in aqueous systems  
18 containing large concentrations of acid.           The  
19 sulfonated polystyrenes which are the preferred embodi-  
20 ment of this invention lose their effectiveness (i.e.,  
21 as a water-in-water pseudo-emulsion former) in salt  
22 water, but are enhanced in acid-containing water.

23           It has been additionally discovered that the  
24 addition of a nonionic surfactant can further enhance  
25 the gelation of the aqueous acid solution. In acidic  
26 solutions, the nonionic surfactant is not needed for  
27 stability (25°C), however, the viscosity of these  
28 pseudoemulsion systems tends to increase significantly  
29 with the addition of small amounts of the nonionic  
30 material (typically <0.04g/l).

31           The nonionic surfactants which can be employed  
32 in the present invention include  
33 polyethylene oxide - polypropylene oxide -  
34 block copolymer (polyols), polyoxyethylene sorbitan

1 fatty acid esters, sorbitan fatty acid esters, fatty  
2 ~~acids and fatty acid derivatives such as ethoxylated~~  
3 fatty acid-Armals (Ethofat<sup>R</sup>), amide derivatives such as  
4 Armals (Ethomid<sup>R</sup>), stearatic acid and stearate deriv-  
5 atives, fluorine-containing nonionic surfactants, fatty  
6 alcohols, alcohol esters, glycinol esters and poly-  
7 ethylene glycol esters. Typical examples of nonionic  
8 surfactants are BASF (Pluronic<sup>R</sup>), ICI (Atlas<sup>R</sup>) ICI  
9 (Bris<sup>R</sup>) and ICI (Arlacel<sup>R</sup>), ICI (Tween<sup>R</sup> series), 3M  
10 (Fluorad<sup>R</sup>) and Shenex (Adol<sup>R</sup>), wherein polyethylene  
11 oxide - polypropylene oxide - block copolymer (polyols)  
12 is preferred. The nonionic surfactant is added to the  
13 solvent system at a concentration of about 0.0001 to  
14 about 1.0 weight percent of total solvent, more prefer-  
15 ably about 0.001 to about 0.5, and most preferably  
16 about 0.001 to about 0.005.

17 In general, the water insoluble ionomeric  
18 polymer will comprise from 10 to 200 meq. pendant  
19 ionomeric groups per 100 grams of polymer, more prefer-  
20 ably from 10 to 100 meq. pendant ionomeric groups.  
21 The ionic groups may be conveniently selected from  
22 carboxylate, phosphonate,  
23 and sulfonate, preferably sulfonate groups. In most  
24 instances, the ionomers utilized in the present inven-  
25 tion are neutralized with the basic materials selected  
26 from Groups IA, IIA, IB and IIB of the Periodic Table of  
27 Elements and lead, tin and antimony, as well as ammonium  
28 and amine counterions. Ionic polymers which are subject  
29 to the process of the present invention are illimitable  
30 and include both plastic and elastic polymers. Specific  
31 polymers include sulfonated polystyrene, sulfonated  
32 t-butyl styrene, sulfonated ethylene copolymers,  
33 sulfonated propylene copolymers, sulfonated styren /  
34 acrylonitrile copolymers, sulfonated styrene/methyl  
35 methacrylate copolymers, sulfonated block copolymers of  
36 styren /ethylene oxide, acrylic acid c polymers with  
37 styrene, sulfonated polyisobutylene, sulfonated ethylene-

1 propylene terpolymers, sulfonated polyisoprene, and  
2 sulfonated elastomers and their copolymers. The pre-  
3 ferred polymers of the present invention are ethylene-  
4 propylene terpolymers and polystyrene, wherein poly-  
5 styrene is most preferred.

6           Neutralization of the cited polymers with  
7 appropriate metal hydroxides, metal acetates, metal  
8 oxides, or ammonium hydroxide etc., can be conducted  
9 by means well-known in the art. For example, the  
10 sulfonation process as with Butyl rubber containing  
11 a small 0.3 to 1.0 mole percent unsaturation can be  
12 conducted in a suitable solvent such as toluene,  
13 with acetyl sulfate as the sulfonating agent, such as  
14 described in U.S. Patent 3,836,511. The resulting  
15 sulfonic acid derivative can then be neutralized with  
16 a number of different neutralization agents such as a  
17 sodium phenolate and similar metal salts. The amounts  
18 of such neutralization agents employed will normally be  
19 equal stoichiometrically to the amount of free acid in  
20 the polymer plus any unreacted reagent which is still  
21 present. It is preferred that the amount of neutraliz-  
22 ing agent be equal to the molar amount of sulfonating  
23 agent originally employed plus 10 percent more to  
24 insure full neutralization. The use of more of such  
25 neutralization agent is not critical. Usually there  
26 is sufficient neutralisation agent to effect at least  
27 50 percent neutralization of the sulfonic acid groups  
28 present in the polymer, preferably at least 90 percent,  
29 and most preferably substantially complete neutralization  
30 of such acid groups should be effected.

31           The degree of neutralization of said ionomeric  
32 groups may vary from 0 (free acid form) to greater than  
33 100 mole percent, preferably 50 to 100 percent. With  
34 the utilization of neutralized ionomers in this present  
35 invention, it is preferred that the degree of neutral-

1    ization be substantially complete, that is with no  
2    substantial free acid present and without substantial  
3    excess of the base other than that needed to insure  
4    neutralization.    The neutralized ionomers possess  
5    greater thermal stability compared to its acid form.  
6    Thus, it is clear that the polymers which are normally  
7    utilized in the present invention comprise substantially  
8    neutralized pendant groups, and in fact, an excess of  
9    the neutralizing material may be utilized without  
10   defeating the objects of the present invention.

11            The ionomeric polymers of the present inven-  
12   tion may vary in number average molecular weight from  
13   1,000 to 10,000,000 preferably from 5,000 to 500,000,  
14   most preferably from 10,000 to 200,000.    These polymers  
15   may be prepared by methods known in the art, for example,  
16   see U.S. Patent 3,642,728.

17            The preferred ionic copolymers for use in the  
18   present invention, e.g., sulfonated polystyrene and  
19   substituted derivatives thereof, may be prepared by  
20   the procedures described in U.S. Patent 3,870,841,  
21   filed October 2, 1972, in the names of H. S. Makowski,  
22   R. D. Lundberg and G. H. Singhal.

23            The water insoluble, ionomeric polymers may be  
24   incorporated into the organic liquid at a level of from  
25   0.01 to 0.5 weight percent and more preferably from 0.01  
26   to 0.4 weight percent, based on the organic liquid and  
27   the polar cosolvent.

28            Specific examples of preferred ionomeric  
29   polymers which are useful in the present invention  
30   include sulfonated polystyrene, sulfonated poly-t-butyl  
31   styrene, sulfonated polyethylene (substantially non-  
32   crystalline), and sulfonated ethylene copolymers,  
33   sulfonated polypropylene (substantially noncrystalline),

1 and sulfonated polypropylene copolymers, sulfonated  
2 styrenemethyl methacrylate copolymers, (styrene)-acrylic  
3 acid copolymers, sulfonated polyisobutylene, sulfonated  
4 ethylene-propylene terpolymers, sulfonated polyisoprene,  
5 sulfonated polyvinyl toluene and sulfonated polyvinyl  
6 toluene copolymers.

7           The ionomeric polymers of the present inven-  
8 tion may be prepared prior to incorporation into the  
9 organic solvent, or by neutralization of the acid form  
10 insitu. For example, preferably the acid derivative is  
11 neutralized immediately after preparation. For example,  
12 if the sulfonation of polystyrene is conducted in solu-  
13 tion, then the neutralization of that acid derivative  
14 can be conducted immediately following the sulfonation  
15 procedure. The neutralized polymer may then be isolated  
16 by means well-known to those skilled in the art, i.e.,  
17 coagulation, steam stripping, or solvent evaporation,  
18 because the neutralized polymer has sufficient thermal  
19 stability to be dried for employment at a later time in  
20 the process of the present invention. It is well-known  
21 that the unneutralized sulfonic acid derivatives do not  
22 possess good thermal stability and the above operations  
23 avoid that problem.

24           It is also possible to neutralize the acid  
25 form of these polymers in situ; however, this is not a  
26 preferred operation, since in situ neutralization  
27 requires preparation of the sulfonic acid in the organic  
28 liquid which is to be subjected to the present process,  
29 or the acid form of the ionic polymer must be dissolved  
30 in said organic liquid. The latter approach may involve  
31 handling of an acid form of an ionic polymer which has  
32 limited thermal stability. Therefore, it is quite  
33 apparent that the preparation and isolation of a neu-  
34 tralized ionic polymer affords the maximum latitude in  
35 formulation, less problems in handling polymers of



1 limited thermal stability and maximum control over the  
2 final mixture of ionic polymer, polar cosolvent and  
3 organic liquid.

4           The organic liquids, which may be utilized  
5 in the present invention, are selected with relation  
6 to the ionic polymer and vice-versa. The organic liquid  
7 may be selected from  
8 aromatic hydrocarbons, cyclic aliphatic ethers, ali-  
9 phatic ethers, organic aliphatic esters and mixtures  
10 thereof.

11           Specific examples of organic liquids to be  
12 employed with the various types of polymers are:

| 13 <u>Polymer</u>           | <u>Organic Liquid</u>        |
|-----------------------------|------------------------------|
| 14 sulfonated polystyrene   | benzene, toluene, ethyl      |
| 15                          | benzene, methylethyl         |
| 16                          | ketone, xylene, styrene,     |
| 17                          | ethylenedichloride,          |
| 18                          | methylene chloride.          |
| 19 sulfonated poly-t-butyl- | benzene, toluene, xylene,    |
| 20 styrene                  | ethyl benzene, styrene,      |
| 21                          | t-butyl styrene, aliphatic   |
| 22                          | oils, aromatic oils, hexane, |
| 23                          | heptane, decane, nonane.     |
| 24 sulfonated ethylene-     | pentane, aliphatic and       |
| 25 propylene terpolymer     | aromatic solvents, oils      |
| 26                          | such as Solvent "100         |
| 27                          | Neutral", "150 Neutral"      |
| 28                          | and similar oils, benzene,   |
| 29                          | diesel oil, toluene,         |
| 30                          | xylene, ethyl benzene,       |
| 31                          | pentane, hexane, heptane,    |

|    |                            |                             |
|----|----------------------------|-----------------------------|
| 1  |                            | octane, isooctane, nonane,  |
| 2  |                            | decane aromatic solvents,   |
| 3  |                            | ketone solvents.            |
| 4  | sulfonated styrene-methyl- | dioxane, halogenated ali-   |
| 5  | methacrylate copolymer     | phatics, e.g., methylene    |
| 6  |                            | chloride, tetrahydrofuran.  |
| 7  | sulfonated polyisobutylene | saturated aliphatic hydro-  |
| 8  |                            | carbons, diisobutylene,     |
| 9  |                            | triisobutylene, aromatic    |
| 10 |                            | and alkyl substituted       |
| 11 |                            | aromatic hydrocarbons,      |
| 12 |                            | chlorinated hydrocarbons,   |
| 13 |                            | n-butyl ether, n-amyl,      |
| 14 |                            | ether, methyl oleate,       |
| 15 |                            | aliphatic oils, oils pre-   |
| 16 |                            | dominantly paraffinic       |
| 17 |                            | in nature and mixtures      |
| 18 |                            | containing naphthenic       |
| 19 |                            | hydrocarbons. "Solvent 100  |
| 20 |                            | Neutral", "Solvent 150      |
| 21 |                            | Neutral" and all related    |
| 22 |                            | oils, low molecular weight  |
| 23 |                            | polymeric oils such as      |
| 24 |                            | squalene, white oils and    |
| 25 |                            | process oils having 60      |
| 26 |                            | percent or less aromatic    |
| 27 |                            | content.                    |
| 28 | sulfonated polyvinyl       | toluene, benzene, xylene,   |
| 29 | toluene                    | cyclohexane, ethyl benzene, |
| 30 |                            | styrene, methylene chlo-    |
| 31 |                            | ride, ethylene dichloride.  |

32                   The process of the present invention includes  
33 incorporating a polar cosolvent, for example, a polar

1 cosolvent in the mixture of organic liquid and water  
2 insoluble ionomer to solubilize the pendant ionomeric  
3 groups. The polar cosolvent will usually have a solubility  
4 parameter of at least 10.0, preferably at least  
5 11.0 and is water miscible and may comprise from 0.1  
6 to 15.0 weight percent, preferably 0.1 to 5.0 weight  
7 percent of the total mixture of organic liquid, water  
8 insoluble ionomeric polymer, and polar cosolvent. The  
9 solvent system of polar cosolvent and organic liquid  
10 in which the water insoluble neutralized sulfonated  
11 (ionomeric) polymer is dissolved contains less than 10  
12 weight percent of the polar cosolvent, more preferably  
13 0.1 to 5.0 weight percent, and most preferably 0.1  
14 to 5.0 weight percent. The viscosity of the solvent  
15 system is less than 1,000 cps, more preferably less than  
16 800 cps and most preferably less than 500 cps.

17 Normally, the polar cosolvent will be a liquid  
18 at room temperature; however, this is not a requirement.  
19 It is preferred, but not essential, that the polar  
20 cosolvent be soluble or miscible with the organic liquid  
21 at the levels employed in this invention. The polar  
22 cosolvent may be selected from water soluble alcohols,  
23 including di- or tri- functional alcohols, amines, amides,  
24 acetamides, phosphates, or  
25 lactones and mixtures thereof. Especially preferred  
26 polar cosolvents are aliphatic alcohols such as methanol,  
27 ethanol, n-propanol, isopropanol, 1,2-propane diol,  
28 monoethyl ether of ethylene glycol, and n-ethylformamide.

29 The amount of aqueous fluid added to the  
30 solution of water insoluble, neutralised or unneutralised  
31 sulphonated polymer, organic liquid and polar cosolvent  
32 having a viscosity of less than 2,000 cps (preferably less  
33 than 200 cps), is 5 to 500 volume percent of water, more  
34 preferably 10 to 300 volume percent water, most preferably  
35 10 to 200 volume percent water.

1           The aqueous acid solution of hydrochloric  
2 acid, in which the water insoluble neutralised or unneutralised  
3 sulphonated polymer thickens, preferably contains less than about 40  
4 weight percent acid, more preferably about 0.1 to about  
5 30 weight percent, and most preferably about 1.0 to  
6 about 20 weight percent.

7

8           The following examples will demonstrate the  
9 performance of sulfonated polystyrene of varying sul-  
10 fonate levels in several specific aqueous environments.

---

11   EXAMPLE 1

12           It has been observed that under certain  
13 conditions, if a hydrocarbon solution containing a low  
14 concentration of a sulfonated polystyrene or sulfonated  
15 EPDM is mildly agitated with water for a short period  
16 of time, a pseudo-emulsion is formed. In the initial  
17 formation stage, the type of pseudo-emulsion produced  
18 in these systems has a continuous aqueous phase while  
19 the hydrocarbon medium is the dispersed phase. It is  
20 believed that the sulfonated polymer stabilizes the  
21 hydrocarbon/water interface. Upon standing for a short  
22 period of time after mixing has occurred, it is observed  
23 that approximately 90 percent of the initial hydrocarbon  
24 solvent can be separated from the system leaving behind  
25 a pseudoemulsion system characterized as a water-in-  
26 water pseudoemulsion. Addition of a small amount of  
27 nonionic surfactant can be added to facilitate this  
28 process. Experimental evidence indicates that free  
29 passage of nonpolar organic solvent occurs through the  
30 sulfonated polymer membrane and the hydrocarbon solvent  
31 is replaced within each sphere by water as the nonpolar,  
32 organic solvent passes through the membrane.

1           As shown in Table I, the essential material  
2 needed for the formation of a pseudo-emulsion system in  
3 a hydrocarbon/water environment is the water insoluble,  
4 neutralized sulfonated polymer. Table I shows that the  
5 addition of water to a No. 2 diesel oil (or xylene)  
6 solution containing tridecyl alcohol as a cosolvent  
7 and/or unsulfonated EPDM (Socabu 55) or polystyrene  
8 (Styron 666) results in a classic phase separation of  
9 the hydrocarbon and water phases. On the other hand,  
10 spontaneous formation of a pseudo-emulsion system occurs  
11 in the presence of the sulfonated polymer. In addition,  
12 it has been observed that more stable pseudo-emulsion  
13 systems are produced with increasing sulfonation level.  
14 The nature of the counterion does not impair the inter-  
15 facial activity of the polymer.

16           Further confirmation of the interfacial  
17 activity of these sulfonated polymers can be obtained  
18 utilizing viscosity measurements. The viscosity of  
19 several water-in-water pseudo-emulsions as a function of  
20 the polymer concentration is shown in Table II. It is  
21 readily apparent that due to the particular "macroscopic"  
22 structures formed in the aqueous phase, significant  
23 viscosification occurs as compared to the dissolution of  
24 a water soluble polymer of equivalent molecular weight  
25 and concentration. The viscosity of the pseudo-emulsion  
26 system at high polymer levels rises, while within the  
27 concentration range between approximately 1 and 5 g/l,  
28 the viscosity is essentially constant. Only when rather  
29 low polymer levels are reached does the viscosity begin  
30 to decline again. A comparison of the EPDM and poly-  
31 styrene data indicates that the nature of the backbone  
32 chain may have little influence on the viscosity of  
33 the system, while the sulfonate level is of paramount  
34 importance. These results can be rationalized by  
35 assuming that the sulfonated polymer resides at the  
36 water-water interface. This latter observation is



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1 supported through the use of light microscopy. Under  
2 low magnification (approximately 100X) the structural  
3 details of the pseudo-emulsion system can be observed.  
4 In the first place, a large number of spheres consti-  
5 tutes a typical pseudo-emulsion system. Secondly, each  
6 pseudo-emulsion particle is a spherical structure in  
7 which a large volume of water is contained with the  
8 polymer film. The continuous phase outside of each  
9 particle is identical in composition to the internal  
10 aqueous phase.

## 11 EXAMPLE 2

12 Table II shows the relationship between the  
13 viscosity of the pseudo-emulsion phase, formed with  
14 polystyrene containing various sulfonation levels,  
15 as a function of polymer concentration. The viscosity  
16 tends to rise at very low polymer concentrations.

17 Outside of this concentration  
18 regime, the viscosity remains constant to rather high  
19 polymer levels ( ~0.5 g/dl.) The viscosity of the  
20 pseudo-emulsion at a particular polymer concentration  
21 does increase with higher sulfonation levels. Undoubt-  
22 edly, this observation is related to both the sphere  
23 size and packing within the aqueous phase.





TABLE I

FORMATION OF WATER-IN-WATER PSEUDO-EMULSION  
(50 HYDROCARBON/50 WATER)

|    | <u>Material</u>                                  | <u>Water/Water<br/>Pseudo-Emulsion Formed</u> |  |
|----|--|---|--|
|    |  |   |  |
| 6  | Tridecyl Alcohol                                 | No  |  |
| 7  | Socabu 55 or Styron 666                          | No  |  |
| 8  | Socabu 55/Tridecyl Alcohol                       | No  |  |
| 9  | Zinc Neutralized (10-30 meq.) EPDM               | Yes   |  |
| 10 | Magnesium and Calcium Neutralized (10 meq.) EPDM | Yes   |  |
| 11 | Magnesium and Calcium Neutralized (10 meq.) EPDM | Yes   |  |
| 12 | Tridecyl Alcohol                                 |   |  |
| 13 | Unneutralized Sulfonated (25 meq.) EPDM          | Yes   |  |
| 14 | Tridecyl Alcohol                                 | Yes   |  |
| 15 | Sodium Sulfonated (1-6 mole %) Polystyrene       | Yes   |  |
| 16 | Zinc Sulfonated (1-3 mole %) Polystyrene         | Yes   |  |

TABLE II  
 VISCOSITY\* - POLYMER CONCENTRATION DATA  
 OF A TYPICAL PSEUDO-EMULSION SYSTEM

|    | Material   | Polymer Concentration<br>(g/l) | Viscosity (cps) |
|----|--|--------------------------------|-----------------|
| 4  | Sulfonated Polystyrene<br>(Sodium Salt - 1.7 mole %) | 0.25                           | 210             |
| 5  |  | 0.5                            | 295             |
| 6  |  | 1.25                           | 315             |
| 7  |  | 2.5                            | 320             |
| 8  |  | 5.0                            | 340             |
| 9  | Sulfonated EPDM<br>(Magnesium Salt - 10 meq.)        | 0.50                           | 160             |
| 10 |  | 1.25                           | 204             |
| 11 |  | 2.5                            | 210             |
| 12 |  | 5.0                            | 210             |
| 13 |  |                                |                 |

17 \*Viscosity measured with a BrookfieldR viscometer at 30 RPM.

TABLE III  
VISCOSITY\* - POLYMER CONCENTRATION DATA OF SEVERAL PSEUDO-EMULSION  
SYSTEMS FORMED WITH SEVERAL SODIUM SALTS OF SULFONATED POLYSTYRENES

|    | <u>Material (mole %)</u> | <u>Polymer Level (g/l)</u> | <u>Viscosity (cps)</u> |
|----|--------------------------|----------------------------|------------------------|
| 1  |                          |                            |                        |
| 2  |                          |                            |                        |
| 3  |                          |                            |                        |
| 4  |                          |                            |                        |
| 5  | 3.0                      | 0.12                       | 280                    |
| 6  |                          | 0.5                        | 430                    |
| 7  |                          | 1.0                        | 480                    |
| 8  |                          | 2.0                        | 490                    |
| 9  | 4.19                     | 0.12                       | 380                    |
| 10 |                          | 0.25                       | 440                    |
| 11 |                          | 0.5                        | 570                    |
| 12 |                          | 2.0                        | 820                    |
| 13 | 6.05                     | 0.12                       | 420                    |
| 14 |                          | 0.25                       | 540                    |
| 15 |                          | 0.5                        | 820                    |
| 16 |                          | 2.0                        | 950                    |

17 \*viscosity measured with a Brookfield<sup>R</sup> viscometer at 30 RPM.

1 EXAMPLE 3

2           Due to the aqueous nature of the fluid within  
3 the thin membrane of the pseudo-emulsion particle, we  
4 observe dramatic changes in viscosity as the shear rate  
5 is modified. Table IV shows the viscosity behavior of  
6 a typical pseudo-emulsion system in fresh water as a  
7 function of the rate of shear. At low shear rates, the  
8 viscosity is high, while a decrease is found at higher  
9 shear. Furthermore, we observe a marked viscosity  
10 decrease as the overall shear rate is increased, which  
11 is typical behavior of all pseudo-emulsion systems (i.e.  
12 ~~fresh, salt, acid or basic environments).~~ In this  
13 particular example, an order of magnitude viscosity  
14 change is found over a relatively modest shear rate  
15 range. Furthermore, we observe that this behavior is  
16 reversible (which again is typical behavior of a pseudo-  
17 emulsion system) within the shear rate range presented  
18 in this example.

TABLE IV

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1           It is evident from these discussions that this  
2 invention claims a markedly different process and  
3 product than that described in some previous patents  
4 covering the same class of polymers in similar mixed  
5 solvents. The prior applications were specifically  
6 directed at gelation of a hydrocarbon phase by contact  
7 of mixed solvents with an aqueous phase and extraction  
8 of a water miscible cosolvent from the organic phase,  
9 thereby permitting association of the ionic groups and  
10 gelation. In this and copending applications, we claim  
11 viscosification of the aqueous phase. Such a claim  
12 would certainly appear inconsistent and unexpected in  
~~13 view of those prior patent applications. This discus-~~  
14 sion will attempt to explain these observations on a  
15 molecular scale.

16           We assume that the ionic polymers of this  
17 study are dissolved in an organic diluent containing  
18 a polar cosolvent (alcohol) via selected solvation.  
19 The resulting ionic polymer is thereby homogeneously  
20 dissolved without substantial aggregation. Now, if  
21 sufficient polymer is present (i.e. >1%) for a conven-  
22 tional high molecular weight polymer, there is an  
23 overlap of the polymer coils (i.e., they intermingle  
24 and entangle). Under these conditions, if the cosolvent  
25 is removed (i.e., by contact with water), then the  
26 resultant aggregation of the ionic groups results in a  
27 total network or polymer gelation of the hydrocarbon  
28 phase occurs.

29           However, the unexpected observation which is  
30 the basis for the present invention is that, if the  
31 polymer concentration in the hydrocarbon phase is less  
32 than 0.5% or so, the polymer coils no longer are in the  
33 overlap regime. Thus, entanglements between polymer  
34 chains do not obtain. Under these conditions, contact  
35 of the solution with water does not result in gelation,

1 but rather the polymer forms the pseudoemulsion phase  
2 described herein. Thus, polymer concentration is the  
3 major variable and dominates which phase (aqueous or  
4 hydrocarbon) is viscosified.

5 EXAMPLE 4

6 Table V shows the effectiveness of 6.05 mole  
7 percent sulfonated polystyrene as a viscosifier for a 10  
8 percent hydrochloric acid solution. The data indicate  
9 that acid solutions containing pseudo-emulsion particles  
10 can be used to significantly enhance the viscosity  
11 of the aqueous acid phase even though the sulfonated  
12 polymer is hydrocarbon soluble. The viscosity of the  
13 hydrocarbon solvent containing the sulfonated polymer is  
14 less than 100 centipoise. The data also show that the  
15 pseudo-emulsion phase can be produced over a wide range  
16 of "dilution" with little change in viscosity. Each  
17 individual sphere is capable of expanding to accommodate  
18 the increased aqueous acid phase volume by absorption  
19 through the polymer membrane. The size of each sphere  
20 increases, but the volume fraction of spheres remains  
21 constant.

TABLE V

VISCOSITY (30 RPM) OF PSEUDO-EMULSION\*  
VERSUS VOLUME OF HCl SOLUTION (10 %)

|   | <u>Solution Volume (ml)**</u> | <u>Viscosity (cps)</u> |
|---|-------------------------------|------------------------|
| 5 | 25                            | 696                    |
| 6 | 30                            | 500                    |
| 7 | 35                            | 384                    |
| 8 | 40                            | 544                    |
| 9 | 45                            | 592                    |

10 \*Initial solution concentrations: 15 ml. at 0.5 g/l of  
11 6.05 mole % sulfo-polystyrene.

12 \*\*Amount of acid solution used to prepare pseudo-emulsion phase.



1 EXAMPLE 5

2           Table VI shows the effectiveness of utilizing  
3 a nonionic surfactant (BASF Pluronic<sup>R</sup> F-108) at very low  
4 concentrations in the preparation of pseudo-emulsions in  
5 10 weight percent acid solution. The sulfonated poly-  
6 styrene was initially dissolved in a xylene/methanol  
7 solvent system. The data indicates that these acid  
8 solutions containing pseudo-emulsion particles in  
9 conjugation with minute amounts of nonionic surfactant  
10 can be used to significantly enhance the viscosity of  
11 the aqueous acid solution even though the polymer is  
12 wholly hydrocarbon soluble. Moreover, the data show  
13 that the surfactant produces marked enhanced viscosity  
14 over that observed without surfactant present (Table V).  
15 The data also show that these pseudo-emulsion systems  
16 can be produced over a wide range of "dilution" with  
17 relatively minor modification in viscosity.

18

TABLE VI

19 VISCOSITY (12 RPM) OF PSEUDO-EMULSION (NaSPS) VERSUS  
20 VOLUME OF HCl SOLUTION (0.04 g/l NONIONIC SURFACTANT)

| 21 | <u>Solution Volume (ml.)*</u> | <u>Viscosity (cps)</u> |
|----|-------------------------------|------------------------|
| 22 | 25                            | 5,831                  |
| 23 | 35                            | 4,582                  |
| 24 | 45                            | 5,831                  |

25 ~~\*Amount of acid solution used to prepare pseudo-emulsion~~  
26 phase. Concentration of acid is 10.0 weight percent.

**CLAIMS:**

1 1. A process for forming a thickened aqueous  
2 fluid, wherein such aqueous fluid is selected from  
3 water and aqueous acid solution<sup>and</sup>  
4 having a viscosity of at least about 50 cps which  
5 comprises .:

6 (a) forming a solvent system comprising an organic  
7 liquid and a polar cosolvent, said polar cosolvent being  
8 less than about 10 weight percent of said solvent  
9 system, the viscosity of said solvent system being less  
10 than about 1000 cps;

11 (b) dissolving a water insoluble, unneutral-  
12 ized or neutralised sulphonated polymer in said solvent  
13 system to form a solution, the concentration of said  
14 unneutralized or neutralised sulphonated polymer in said  
15 solution being about 0.01 to about 0.5 weight percent, the  
16 viscosity of said solution being less than about 2000  
17 cps; and

(c) adding about 5 to about 500 volume percent of said aqueous fluid to said solution, said aqueous fluid being immiscible with said solution and with said polar cosolvent wherein said water insoluble, neutralised sulphonated polymer transfers from said organic liquid to said aqueous fluid causing the viscosity of said aqueous fluid to increase to at least 50 cps.

25           2. A process according to claim 1 which  
26 includes a means for removing said organic liquid from  
27 said aqueous fluid.

28 3. A process according to either of claims 1 and 2 wherein  
29 said unneutralized or neutralized sulfonated polymer has

1        about 10 (free acid) to about 200 meq. of pendant  $\text{SO}_3\text{H}$  groups per  
2        100 grams of polymer.

3            4.     A process according to any one of the preceding claims  
4        wherein the sulphonate groups are neutralised with a metal counterion  
5        selected from antimony, tin, lead and Groups IA, IIA, IB or IIB of  
6        the Periodic Table of Elements.

7            5.     A process according to any one of the preceding claims  
8        wherein said neutralised sulphonated polymer is formed from an  
9        elastomeric or thermoplastic polymer.

10           6.     A process according to any one of the preceding claims  
11        wherein said polar cosolvent is selected from aliphatic amines,  
12        mono-, di or tri- functional aliphatic alcohols, water miscible  
13        amides, acetamides, phosphates, lactones and mixtures thereof.

14           7.     A process according to any one of the preceding claims  
15        wherein said organic liquid is selected from aromatic hydrocarbons,  
16        ketones, chlorinated aliphatic hydrocarbons, aliphatic hydrocarbons,  
17        cyclic aliphatic ethers, aliphatic ethers, organic aliphatic esters  
18        and mixtures thereof.

19           8.     A process according to any one of the preceding claims  
20        wherein said aqueous fluid has a nonionic surfactant incorporated therein.

21           9.     A process according to claim 8 wherein said nonionic  
22        surfactant is selected from BASF (Pluronic<sup>R</sup>), ICI (Atlas<sup>R</sup>) ICI  
23        (Bris<sup>R</sup>) and ICI (Arlacel<sup>R</sup>), ICI (Tween<sup>R</sup> series), 3M (Fluorad<sup>R</sup>) and  
24        Shenex (Adol<sup>R</sup>), preferably polyethylene oxide - polypropylene oxide -  
25        block copolymer (polyols).

26           10.    A process according to any one of the preceding claims  
27        wherein the viscosity of the solvent system is less than 100 cps and  
28        the viscosity of the solution formed by dissolving the polymer in  
29        said solvent system is less than 200 cps.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0093596

Application number

EP 83 30 2437

| DOCUMENTS CONSIDERED TO BE RELEVANT  |  |  |  |
|--|--|--|--|
| Category   | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)   |
| X  | US-A-4 282 130 (R.D. LUNDBERG et al.)<br>* Column 1, lines 10-27; column 4, lines 31-53; column 7, lines 52-62 *                 | 1,3-7  | C 08 J 3/08<br>C 08 L 57/06<br>B 01 J 13/00  |
| X  | US-A-4 322 329 (R.D. LUNDBERG et al.)<br>* Column 1, lines 14-31; column 4, lines 36-58; column 6, lines 9-20 *                  | 1,3-7  |  |
| A  | US-A-4 313 862 (R.D. LUNDBERG et al.)<br>* Column 1, lines 15-28; column 4, lines 10-39; column 5, line 59 - column 6, line 68 * | 1,4,5,7  |  |
| A  | US-A-3 770 682 (HUBBARD et al.)<br>* Column 6, lines 58-69 *   | 1  | TECHNICAL FIELDS SEARCHED (Int. Cl. 3)<br><br>C 08 J<br>C 08 L<br>C 09 D<br>C 09 K<br>E 21 B<br>B 01 J |
| The present search report has been drawn up for all claims   |  |  |  |
| Place of search<br>THE HAGUE   |  | Date of completion of the search<br>14-07-1983 | Examiner<br>KERRES P.M.G.  |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>&amp; : member of the same patent family, corresponding document</p> |  |  |  |